The Ohio State University Chemical & Biomolecular Engineering
Honors Thesis

Oxygen Carrying Particle Characterization in Lignocellulosic Fueled Chemical Looping

Written by: Cornelius Cilliers

Honors Thesis Committee:

Dr. Liang-Shih Fan

Dr. James Rathman

Abstract

The growing awareness of climate change due to anthropogenic CO_2 emissions has started a search for clean and renewable energy sources. The chemical looping process is an emerging technology that has potential for high energy efficiency and simultaneous carbon capture. Chemical looping has primarily been demonstrated by using nonrenewable coal as the fuel source. In the future however, using lignocellulosic biomass as the primary fuel could result in a clean and renewable energy source. Fundamental to the chemical looping process are oxygen carrying (OC) particles. These OC particles commonly consist of a metal oxide, which bind oxygen, and an inert support, used to increase mechanical strength and long-term usability. Optimizing the composition of the OC particles for high oxygen carrying capacity, high reactivity, long-term recyclability, high attrition resistance, and low cost is important to achieving economic efficiency and environmental friendliness for the process. Using thermogravimetric analysis the reduction-oxidation reactions of several compositions of OC particles and their reactions with biomass were studied. From the metal oxides Fe_2O_3, CuO, and NiO and two support materials, it was determined that the Fe_2O_3 and NiO mixtures showed optimum characteristics for biomass chemical looping combustion. Gaining understanding of the reaction characteristics of different oxygen carrying particles and interactions with biomass is fundamental to extending the chemical looping process to lignocellulosic materials and the development of a clean, renewable energy process.

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1. Introduction

Energy production from the combustion of carbonaceous fuels has been used by mankind for years and is ubiquitous in society today. Until recently, however, with the development of climate science and a growing awareness of climate change, the overall impact of the unregulated use of carbonaceous fuels was not fully recognized. Environmental and climate scientists now almost unanimously agree that anthropogenic emission of CO_2 is causing global climate change through the greenhouse gas effect[1]. Since after the Industrial Revolution in the late 1800's, there has been a large increase in atmospheric CO_2 concentration from below 300 ppm in 1880 to 370 ppm in 2004[2]. The atmospheric CO_2 concentration levels are continuing to increase at rates greater than 1.5 ppm each year, and projections indicate that if CO_2 mitigation techniques are not employed the total CO_2 concentration could increase to 500 ppm by 2050[2]. Figure 1 depicts the correlation between the rising CO_2 concentration and the corresponding increase in average global temperature.

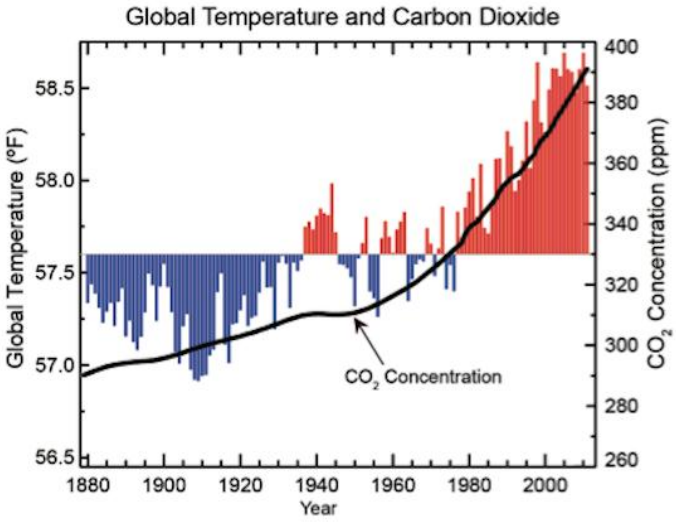

Figure 1: Global surface temperature and atmospheric CO_2 concentration over time[2]

CO_2 emissions to the atmosphere have contributed to climate change through the phenomena known as the greenhouse gas effect[1,2,3] . As the suns electromagnetic radiation passes through the earth's atmosphere a portion of it is emitted back into space while the rest is absorbed, thus causing the earth to retain heat. Consequently, rising CO_2 concentrations have led to the effect known as global warming by retaining increasing amounts of heat from the sun. Since 1895 the U.S. surface temperature has risen approximately 1.5°F, and the temperature is projected to rise between 3°F and 10°F by the end of the century, depending on the extent of carbon emission mitigation[2]. However, these rising CO_2 concentrations do not simply mean increasing surface temperatures. These emissions are causing global climate change and effects such as increases in ocean water temperatures, decreased ocean pH, rising sea levels, reductions in glaciers, and increased frequency of severe storms are just the beginning of potential consequences[1,2,3]. These changes in climate could have dangerous consequences to human health and natural ecosystems, such as flooding, more frequent natural disasters, ocean acidification, wildfires, loss of wetlands, loss of biodiversity, and droughts. Even in the past year, the United States has witnessed some of these meteorological effects with droughts in the Midwest farming, immense wildfires raging across West, and severe hurricanes and snow storms hitting all along the East coast. While these events cannot directly be attributed to climate change, climate scientists predict that the frequency of such natural disasters will increase due to global warming[3]. Thus, without proper control of CO_2 emissions, the global climate will continue to worsen over the coming years.

Coal combustion accounts for nearly half of the electrical energy produced in the United States[4]. However, coal combustion contributes significantly to the greenhouse gas effect by producing immense quantities of CO_2. It is estimated that coal alone accounts for over 1 billion

tonnes of CO_2 per year in the U.S. alone[5]. Due to the growing concern over climate change, determining a method for mitigating anthropogenic CO_2 emissions by capture and sequestration is becoming increasingly important. Recently, there has been a growing interest in chemical looping combustion as a potential method for the capture and separation of CO_2 from the coal combustion process because of its potential for high efficiency. This technology has already been shown to be successful at the pilot scale, and scale-up is in progress[6]. While the chemical looping process has shown great efficiency burning coal, the fact still remains that coal is a nonrenewable energy source. Another exciting prospect is using lignocellulosic biomass as the fuel source. Doing this would result in a renewable energy source, while still benefitting from the efficiency and inherent CO_2 capture found in the chemical looping combustion process. The chemical looping combustion processes of coal and biomass are further discussed in the following section.

1.1 Chemical Looping Overview

The chemical looping combustion process is emerging as one of the most promising alternatives for obtaining clean energy through combustion of carbonaceous energy sources, such as coal and biomass. For this study the two major chemical looping processes that will be considered are syngas chemical looping, and direct chemical looping. These processes have the potential to provide energy more efficiently and cleanly compared to other carbon capture technologies[7]. Figure 2 shows the The U.S. Department of Energy ranking of potential technologies for carbon capture[7]. In this figure the chemical looping process is shown as one of the most promising technologies for cost reduction, although still far from commercialization.

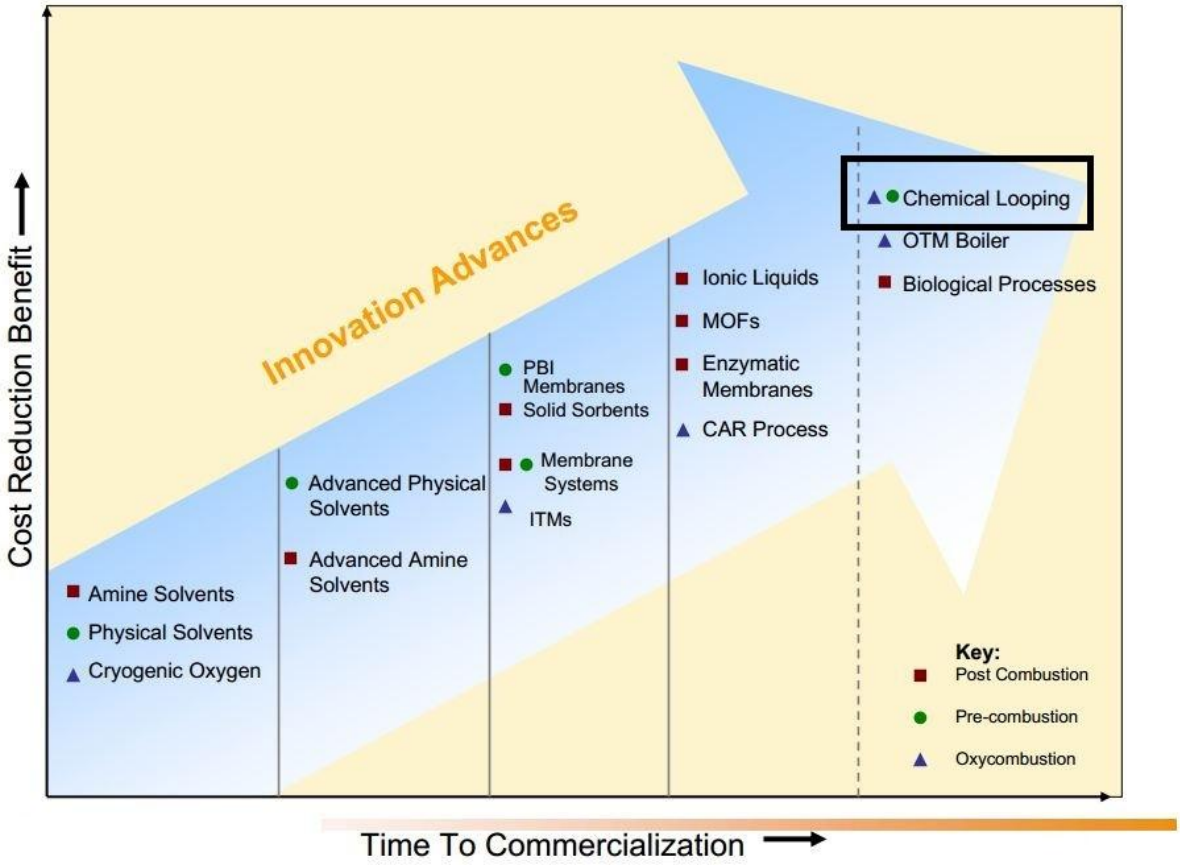

Figure 2: U.S. DOE ranking of potential carbon capture technologies

In general, chemical looping combustion works by looping metal oxide oxygen carrying particles (depicted as Me and MeO) between a reducer reactor and an oxidizer reactor as shown in Figure 3. Fuel is fed into the reducer where it is undergoes combustion by reacting with oxygen from the oxygen carrying particles, thus reducing the metal oxide and releasing CO_2 and H_2O. After combustion the metal oxides (which are now reduced and depicted as Me) are sent to the oxidizer to be re-oxidized by reacting with air. After oxidation the particles are then regenerated and ready to be reused in the reducer reactor.

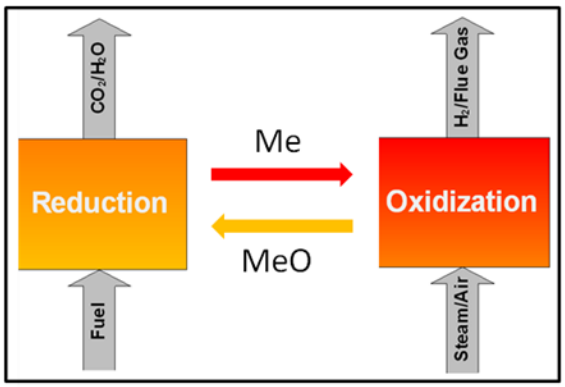

Figure 3: General schematic for chemical looping combustion[8]

To further elucidate the chemical looping combustion process the syngas chemical looping and direct chemical looping processes will be examined. Syngas chemical looping starts with the gasification of fuel into a synthesis gas (syngas) which consists of mostly CO and H_2, and other components including, H_2O and CO_2. Once the syngas is formed it undergoes cyclic reduction-oxidation reactions with the oxygen carrying metal oxide particles, similar to the general schematic described above. A detailed schematic of the process using coal as the fuel source is shown in Figure 4.

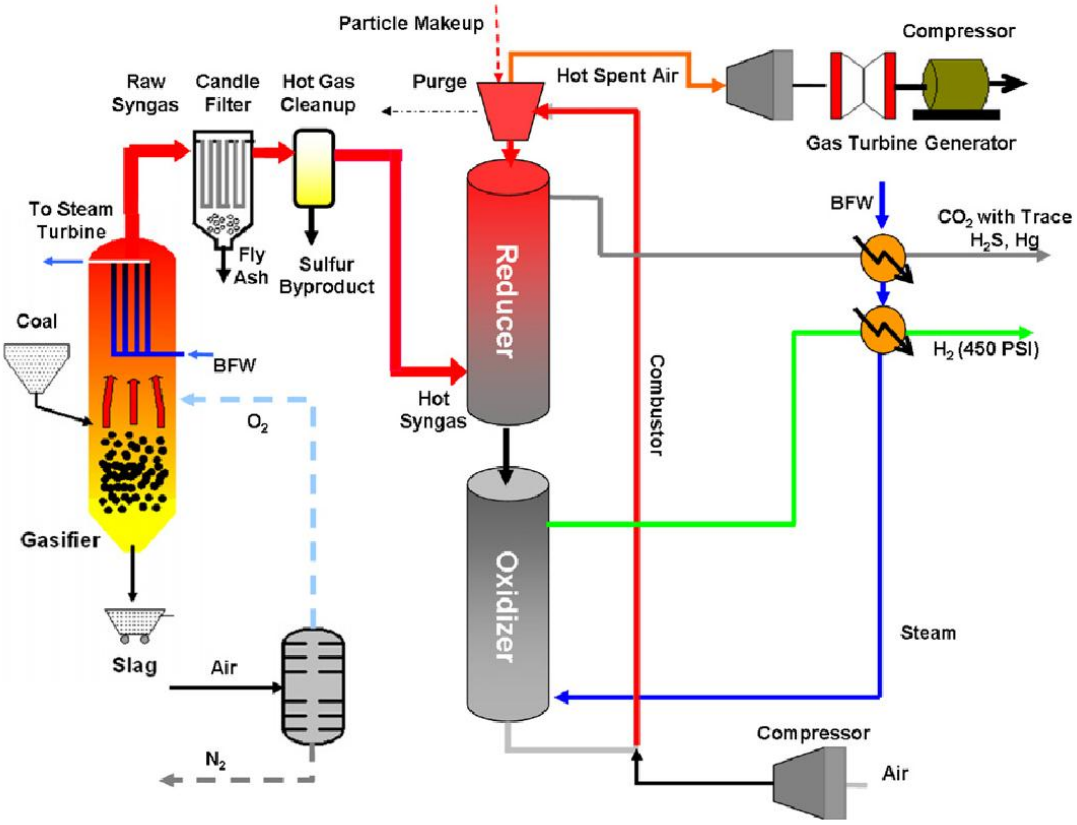

Figure 4: Coal Syngas Chemical Looping General Schematic[9]

First the fuel (in this case coal) is fed into a gasifier unit where it is heated and reacted with small amounts of O_2 and steam. This generates products according to reaction (1) and subsequently goes through the water-gas shift reaction, shown in reaction (2).

$$3C + O_2 + H_2O \rightarrow 3CO + H_2 \quad (1)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (2)$$

These reactions result in CO and H_2 (with some H_2O and CO_2) fed through subsequent cleanup steps and into the reducer reactor. Once in the reducer, the syngas undergoes a reduction reaction with the metal oxide particles. These reactions are described in reactions (3) and (4) below, where "MeO" refers to a general metal oxide particle, and "Me" refers to the reduced metal oxidation state. These reduction reactions generate a gaseous stream of CO_2 and H_2O. Then, after condensing out the H_2O, a pure stream of CO_2 remains, which can be captured and sequestered.

$$MeO + H_2 \rightarrow Me + H_2O \quad (3)$$

$$MeO + CO \rightarrow Me + CO_2 \quad (4)$$

Once the particles are finished reacting in the reducer they move to the oxidizer and are re-oxidized according to reaction (5). Also, a novel feature of the syngas process is the potential to produce a highly pure stream of H_2. This is done by feeding steam into the oxidizer (instead of O_2) and exploiting the reverse reaction of reaction 3, which is shown in reaction (6).

$$Me + 1/2O_2 \rightarrow MeO \quad (5)$$

$$Me + H_2O \rightarrow MeO + H_2 \quad (6)$$

The particles are then pneumatically conveyed up a riser with air, thus ensuring full oxidation, and fed back into the reducer. Just before the reducer there is a small purge to remove any fines or spent particles and a makeup feed to replace any lost particles. The process described above has been demonstrated at the sub-pilot scale here at the Ohio State University and have been shown to effectively capture CO_2 from the combustion of coal[6].

The success of coal using this technology prompted the idea of using a renewable source, such as lignocellulosic biomass, as the primary fuel. Biomass production in the United States alone is 1.3 billion dry tonnes, which could help offset U.S.'s dependence on coal[10]. Using the gasification of biomass would result in a similar process to the coal-based syngas chemical looping. Biomass would be gasified into CO and H_2, resulting in the same feed into the process. Then the same redox reactions carried out with the metal oxide particles would be used, and CO_2 could still be captured.

Another highly efficient process of chemical looping combustion being researched is called direct chemical looping combustion. Direct chemical looping consists of feeding a fuel source into the reducer where it undergoes a series of reactions similar to syngas chemical looping. This process has potential for both coal and biomass as fuel sources[11]. Figure 5 shows the reactions that occur in the reducer, which include reduction, devolatilization, and gasification, when using biomass as the feedstock. In this figure, the metal oxide used was iron oxide, however, other metal oxides are still candidates.

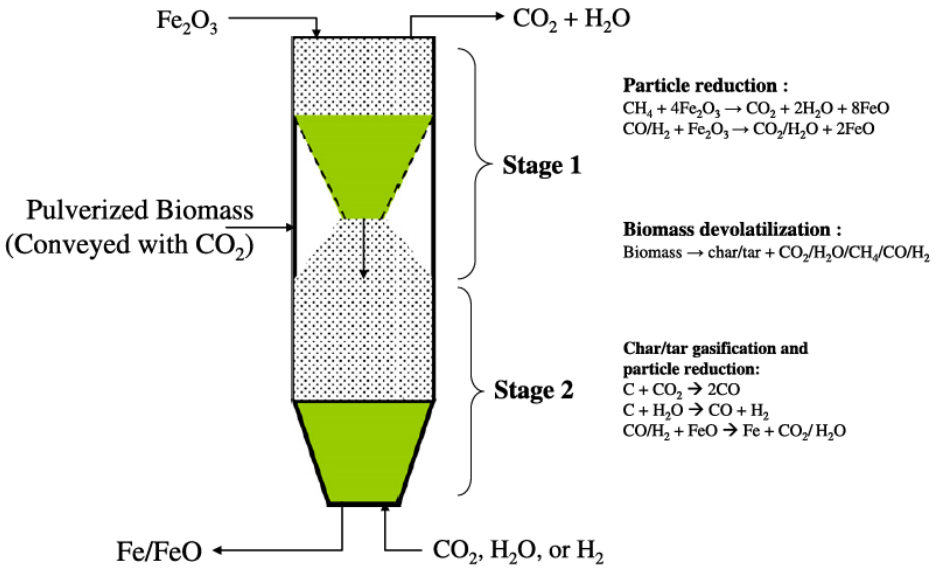

Figure 5: Biomass moving bed reducer design[12]

In this set up, biomass is pneumatically conveyed into the middle of the reducer where it first undergoes devolatilization and then gasification as the biomass char and metal oxide particles move downwards through the reactor. Devolatilization and gasification of biomass results in the formation of char/tar, which reacts with CO_2 and H_2O to form syngas. This syngas, similar in composition to the one produced in the syngas process, as well as a stream of methane (resulting from the decomposition of tars) then reduce the metal oxide particles at the top of the reactor. This then forms CO_2 and H_2O, and after water is condensed, a pure stream of CO_2. Exiting the bottom reactor then are the reduced particles and leftover biomass ash. After exiting the reducer, the solids are then sent to the oxidizer to re-oxidize the metal oxide particles and then pneumatically convey them back into the reducer. Figure 6 shows a schematic for using coal in direct chemical looping. The oxidation reactions and cycling of particles is similar to the syngas chemical looping process.

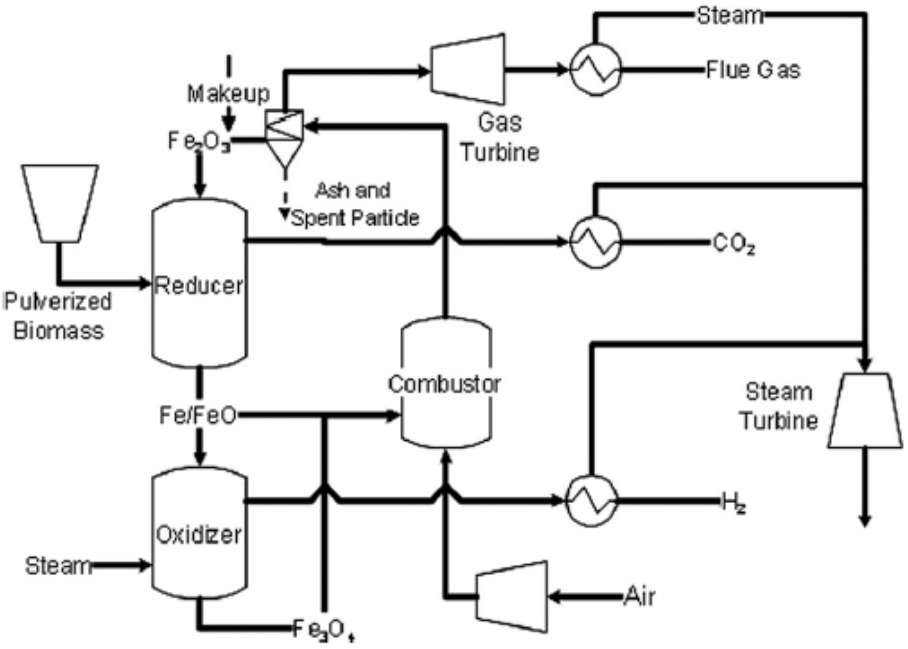

Figure 6: Biomass direct chemical looping schematic[11]

Fundamental to both chemical looping processes are the oxygen carrying metal oxide particles. Optimizing these particles is a large area of study in the field of chemical looping and this will be discussed further in the following section.

1.2 Oxygen Carrying Particles

At the heart of the chemical looping combustion process is the oxygen carrying particles. In order to achieve high process efficacy the particles must exhibit at least some of the following characteristics: high oxygen carrying capacity, high reactivity, long-term recyclability, high attrition resistance, low cost, carbon deposition resistance, and environmental friendliness[8,13,14]. If the particles do not meet at least some of these criteria then the process economics quickly becomes unfavorable. Having a high oxygen carrying capacity is important because the more

oxygen that the particle can carry the less overall volume of particles that will be needed. High reactivity is needed to ensure that the particles can reduce and oxidize quickly, thus shortening the residence time in each reactor. Also, the particles need to maintain this level of reactivity over many cycles to minimize the cost of replacing the particles. Since these particles will be continuously looped, it is important that they are robust and mechanically strong enough to withstand impact forces of entrainment and attrition caused by friction. If the particles are too weak, they will break during the looping cycle and generate fines in the reactor system. Excessive fines in the system are undesirable because they can cause clogging. Also, the fine particles exit the purge easier than the normal-sized particles, thus resulting in more of the oxygen carriers leaving the system and increasing operational expenses. Therefore it is advantageous to have reactive and resilient particles as it helps improve the efficiency and economic feasibility of the chemical looping process[8].

Extensive work has been done to find oxygen carrying particles that fulfill the previously described characteristics. The metal oxides of iron, nickel, copper, manganese, and cobalt have been studied and are capable of going through the cyclic reactions needed in the chemical looping process[14]. The metal oxides of Ni are known to exhibit thermal stability over a wide range of temperatures and also high reactivity with gases; however, they are also high in cost and toxic[15,16]. The metal oxides of Cu also have high reactivity, however, they do not exhibit thermal stability and tend to form agglomerations[17]. Iron oxides are inexpensive, however, the reactivity is lower than both Ni and Cu. The general characteristics of these different metal oxides show that an ideal particle will require optimization of numerous different factors[8].

While the above metal oxides exhibit the desired redox reactivity, they do not form strong particles when sintered. To increase the mechanical strength of the particles, they are

often impregnated with a non-reactive support material. Common choices for these supports include Al_2O_3, TiO_2, MgO, SiO_2, and ZrO_2, however, the list of tested materials is extensive[13]. These supports have been shown to not only increase mechanical strength but also the overall reactivity of the particles. The support materials have been shown to increase the surface area available for reaction, act as a binder to increase strength, and increase the ion permeability by acting as an ion conductor[18]. Therefore, selection of the correct support material is just as important as the metal oxide[18]. Table 1 shows general characteristics of the metal oxides that will be used in this study, where "+" indicates positive attributes, "~" indicates neutral, and "-" indicates undesirable characteristics.

Table 1: General Characteristics of metal oxides[8]

Characteristic	Fe_2O_3	NiO	CuO
Cost	+	-	-
Thermodynamics - Reduction - Steam Oxidation	+ +	+ ~	+ -
Kinetics/Reactivity	-	+	+
Melting Points	+	~	-
Strength	+	-	~
Environmental & Health	~	-	-

The focus of this study will examine various compositions of metal oxide particles and supports to compare various characteristics of oxygen carrying particles. The overall oxygen carrying capacity, oxidation-reduction profiles, percent reduction, rates of reduction, long-term redox behavior, and reactivity with biomass of different oxygen carrying particles will be compared. This will focus on how composition affects reactivity rather than the physical strength

and attrition resistance, however, these considerations will be important in eventually choosing an ideal oxygen carrying particle.

2. Experimental Methodology

2.1 Mixture Preparation

A screening experiment was designed to test a variety of mixture compositions of metal oxide and supports to compare relative reactivities. Iron oxide (Fe_2O_3), nickel oxide (NiO), and copper oxide (CuO) were the three metal oxides used. Two support materials were used and will be referred to by the code S1 and S2 to prevent dissemination of any proprietary information. Each metal oxide was used with each support at three different weight percent ratios of 25:75, 50:50, and 75:25, for a total of 18 separate trials. Usually, similar amounts of metal oxide and support are used, however, one focus of this study is to see how more extreme compositions (greater than 40:60 weight percent) affect the reactivity of the particles.

The mixtures were mechanically mixed together and then sintered. The Fe_2O_3 and NiO mixture were sintered at 1000 °C for 12 hours. The CuO particles were sintered at 800 °C for 12 hours, due to the melting point of CuO occurring just above 1000 °C. Sintering the CuO mixtures at high temperatures would result in copper melting and fusing with the crucibles, rendering it unusable. Although sintered at a different temperature, the value 800 °C is in accordance with literature values for sintering CuO and was deemed usable for the experiment[17]. The process of mechanical mixing was used due to its combination of economic efficiency and ease of use. While mechanical mixing gives less homogeneity than other methods,

such as freeze granulation, particles made using this method have exhibited high reactivity for numerous cycles[8]. The sintering/calcination step is commonly used to promote binding between the metal oxide and the support, thus increasing the mechanical strength of the particles.

In other experiments in literature the mixtures are often pelletized, however, for the screening experiment it was deemed unnecessary to do this. Pelletizing the particles does not change the reactivity of the particles as significantly as sintering, and for the purpose of screening based upon redox reactivity this was unnecessary. Understanding the kinetics of the redox reactions and the effect of the biomass was the focus of this study.

2.2 Thermogravimetric Analysis

A thermogravimetric analyzer (TGA) was used to measure the reactivity of the different mixtures over a set number of cycles of reduction and oxidation at 900 °C (800 °C for CuO mixtures). These values were used to mimic the conditions in the reactors. When screening the particles only 3 cycles were used. Each cycle started with flushing using nitrogen gas (N_2), then cycled through reduction with hydrogen gas (H_2), flushing with N_2 again, oxidation with air for 30 min, and flushing again with N_2. The initial flushing step is required to ensure that the mixture is in an inert environment while the TGA heats up, thus preventing any unwanted reactions to occur. The middle flushing steps were done for safety reasons to ensure no combustion between H_2 and air would occur. Periods of reduction and oxidation were chosen at 30 min to allow for full reduction and oxidation to be achieved. The flow of all three gases was set to 100 mL/min (STP). A typical experiment would look like the outline on the next page.

1. Warm up and flushing (25 min)
2. Reduction with H_2 (30 min)
3. Flushing with N_2 (5 min)
4. Oxidation with air (30 min)
5. Flushing with N_2 (5 min) and repeat steps 2 through 5 for set number of cycles.
6. Cool down and flush (25 min)

After the screening phase where many compositions were tested, fresh mixtures of the 50:50 weight percent compositions were run for more cycles to see how the reduction-oxidation profile changes over a larger number of cycles. All 6 of these compositions were tested for 10 cycles, and the compositions containing S2 as the support were used for even longer tests of 20 cycles. The cycles used in each of these tests were under identical conditions to the shorter 3 cycle tests.

The TGA itself uses a small crucible to hold the mixture in the middle of a 15 mm diameter glass reactor. The reactor is surrounded by a protective gas (helium) and enclosed by heaters. The weight of the sample and the temperature of the reactor are recorded through a computer software data capturing system. By examining the change in weight over time the degree of reduction or oxidation can be determined.

In addition to the particle characterization tests, reactivity in the presence of biomass was also tested. For these trials devolatilized biomass was mechanically mixed with freshly sintered powder and allowed to react for 1 cycle. The six 50:50 weight percent compositions of the different metal oxides and supports were cycled for one cycled with biomass char to see if reactivity significantly changed.

Devolatilized biomass was used in order to prevent any unwanted side reactions with aromatic hydrocarbons from occurring with the particles. Also, these aromatic hydrocarbons that are produced produce a health risk since many are known to be cancerous. While these reactions are important to understand for the biomass direct chemical looping process, they are beyond the scope of this study. In order to devolatilize the biomass, it was placed in a furnace and heated to 900 °C for 2 hours with N_2 gas flow to ensure inert conditions to prevent combustion from occurring. After devolatilization, the biomass should be composed of carbon and ash.

3. Results and Discussion

3.1 Oxygen Carrying Capacity

Using the TGA output, the weight over time was measured for all trials. From this, the percent weight change over time could be calculated. For each sample there was a different theoretical maximum weight change that could occur, which depended on the amount of metal oxide. This value was calculated using three assumptions. First, it was assumed that the support material was completely inert, and did not undergo any redox reactivity. Second, it was assumed that the mechanical mixing gave a completely homogeneous mixture that exhibited the desired composition. Thirdly, it was assumed that all the metal oxide in the mixture would fully reduce (lowest oxidation state of the metal). Table 2 below shows the theoretical maximum percent weight change that could occur for the different compositions. Since the support materials are considered inert they are not included in the compositions on the following page.

Table 2: Oxygen carrying capacities of various metal oxides and compositions

Composition (% MO)	Metal Oxide (Initial State)	Metal Oxide (Reduced State)	Extent of Maximum Weight Change
25%	Fe_2O_3	Fe	7.51%
50%	Fe_2O_3	Fe	15.02%
75%	Fe_2O_3	Fe	22.54%
25%	NiO	Ni	5.36%
50%	NiO	Ni	10.71%
75%	NiO	Ni	16.07%
25%	CuO	Cu	5.03%
50%	CuO	Cu	10.07%
75%	CuO	Cu	15.08%

From this it is clear that Fe_2O_3 compositions have the greatest theoretical oxygen carrying capacity, followed by NiO and CuO. Oxygen carrying capacity is an important aspect of the oxygen carrying particles because it determines the amount of particles needed. Lower capacities result in the need for more particles, which results in increased costs and also increased reactor size.

3.2 Three Cycle Testing

Since the theoretical maximum weight change that could occur corresponds to the particle being fully reduced, this value was used to calculate the percent reduction for all compositions of metal oxide and support. The calculation used to find the percent conversion is shown in equation (7)[19].

$$C_t = \frac{W_i - W_t}{W_i - W_x} * 100\% \quad (7)$$

Here C_t represents the sample conversion, W_i is the initial weight of the sample, W_t is the instantaneous weight, and W_x is the calculated weight corresponding to full reduction of the particle. The typical behavior shown by all the particles is shown in Figure 7 below. Here the values close to 100% correspond to full reduction while the values close to 0% represent full oxidation. The slight bumps correspond to changes in gas flow rate from the TGA and can be ignored. It should be noted that the percent oxidation could also have been calculated, however, the oxidation reactions tend to occur significantly faster and go to completion faster, as evident from Figure 7. Thus, the reduction reactions are of more interest because they are more time limiting than oxidation.

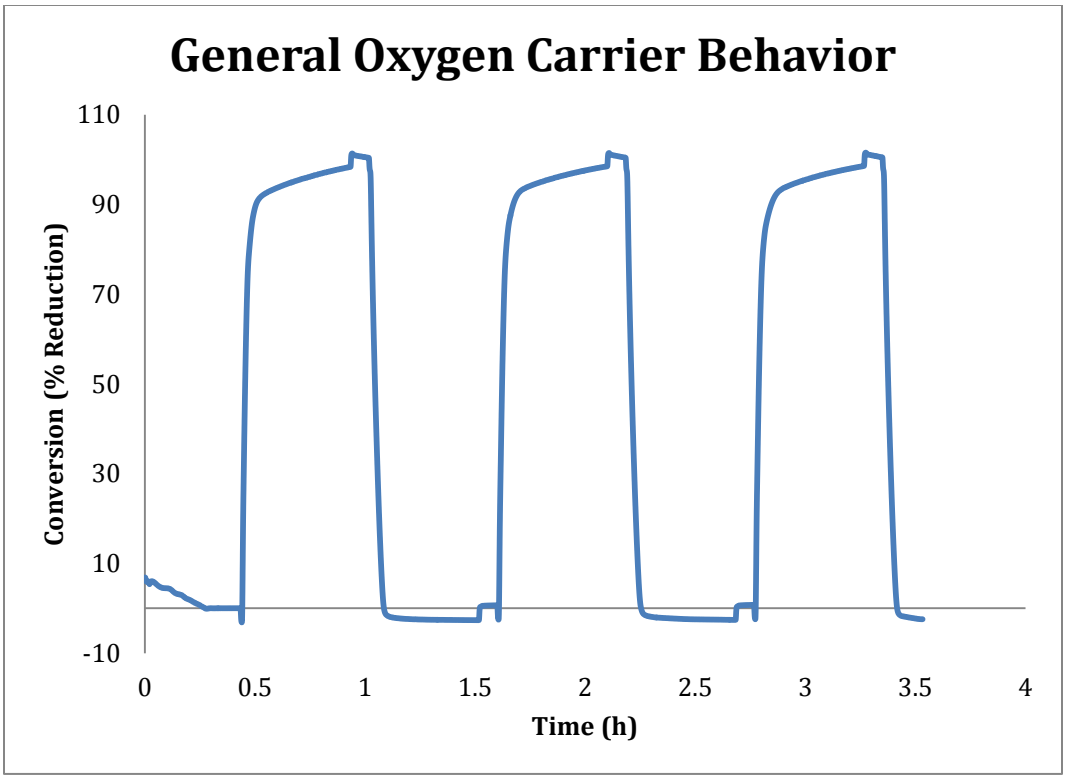

Figure 7: General Reduction-Oxidation Curve Over 3 Cycles

Also of note in Figure 7, is the tendency for the particle to become activated by the third cycle. This is evident from the slightly higher reduction achieved in the third cycle. For this reason, only the third cycle was compared for each composition. Figures 8, 9, and 10 show the reduction curve for the third cycle for the iron oxide, nickel oxide, and copper oxide compositions, respectively. In these figure the curves are labeled with the metal used in the metal oxide and support, and the numerical values correspond to weight percentages of the respective material.

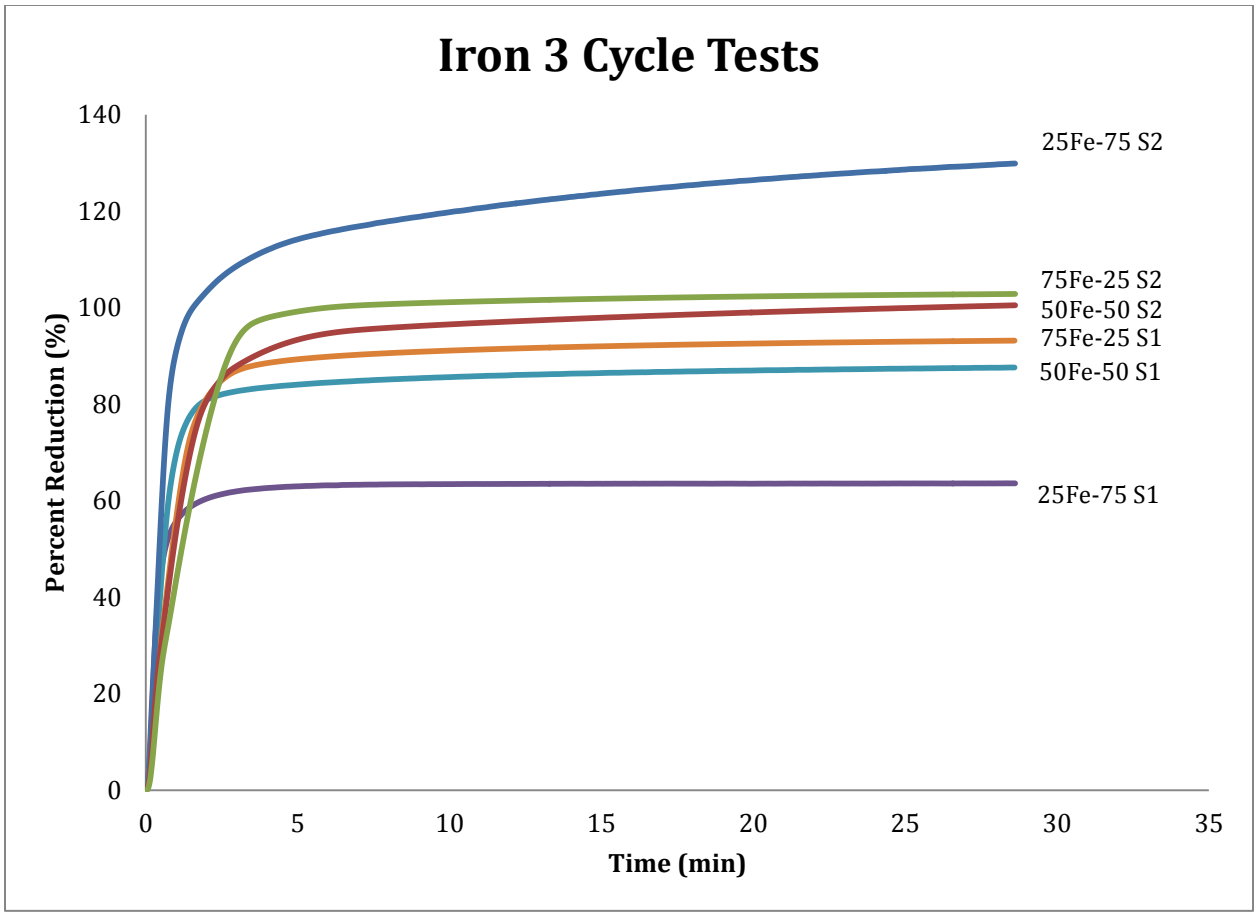

Figure 8: 3 Cycle Tests using Iron Oxide Compositions

In the iron oxide tests, the Fe –S2 compositions showed the best overall reduction characteristics. These compositions reduced faster and achieved higher levels of reduction than the S1 compositions. Generally, the higher the percentage of iron in the composition meant a greater overall reduction was achieved. The only exception to this was the case of 25%Fe – 75%S2, which achieved reduction much higher than the theoretical 100%. This result is discussed in possible sources of error at the end of this section. The rate of reduction in the iron compositions was relatively high, taking between 3 and 7 minutes to achieve near full reduction. Rates for both S1 and S2 mixtures were comparable, with S2 being slightly higher.

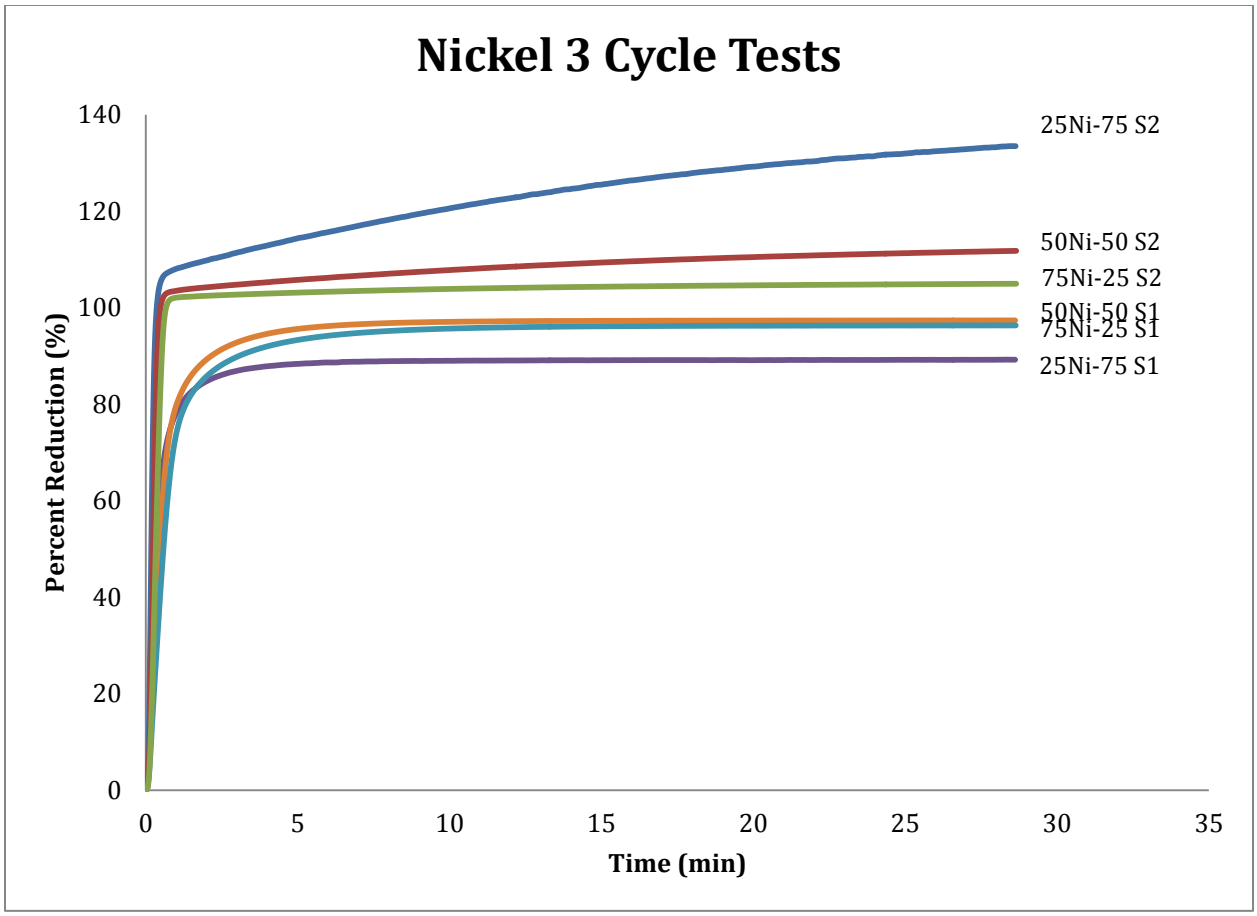

Figure 9: 3 Cycle Tests using Nickel Oxide Compositions

In the nickel composition tests, S2 based supports again showed higher levels of reduction at faster rates in each case. Similar to the iron oxide results, the 25%Ni – 75%S2 compositions showed levels of reduction much higher than the theoretical maximum. Also the 50%Ni – 50%S2 and 75%Ni – 25%S2 showed overall reduction higher than the theoretical maximum. This trend of S2 compositions exhibiting higher than the theoretical maximum reduction shows that S2 could exhibit some redox reactivity. The S2 compositions achieved near full reduction in approximately two minutes compared to the S1 compositions which took between three and five minutes.

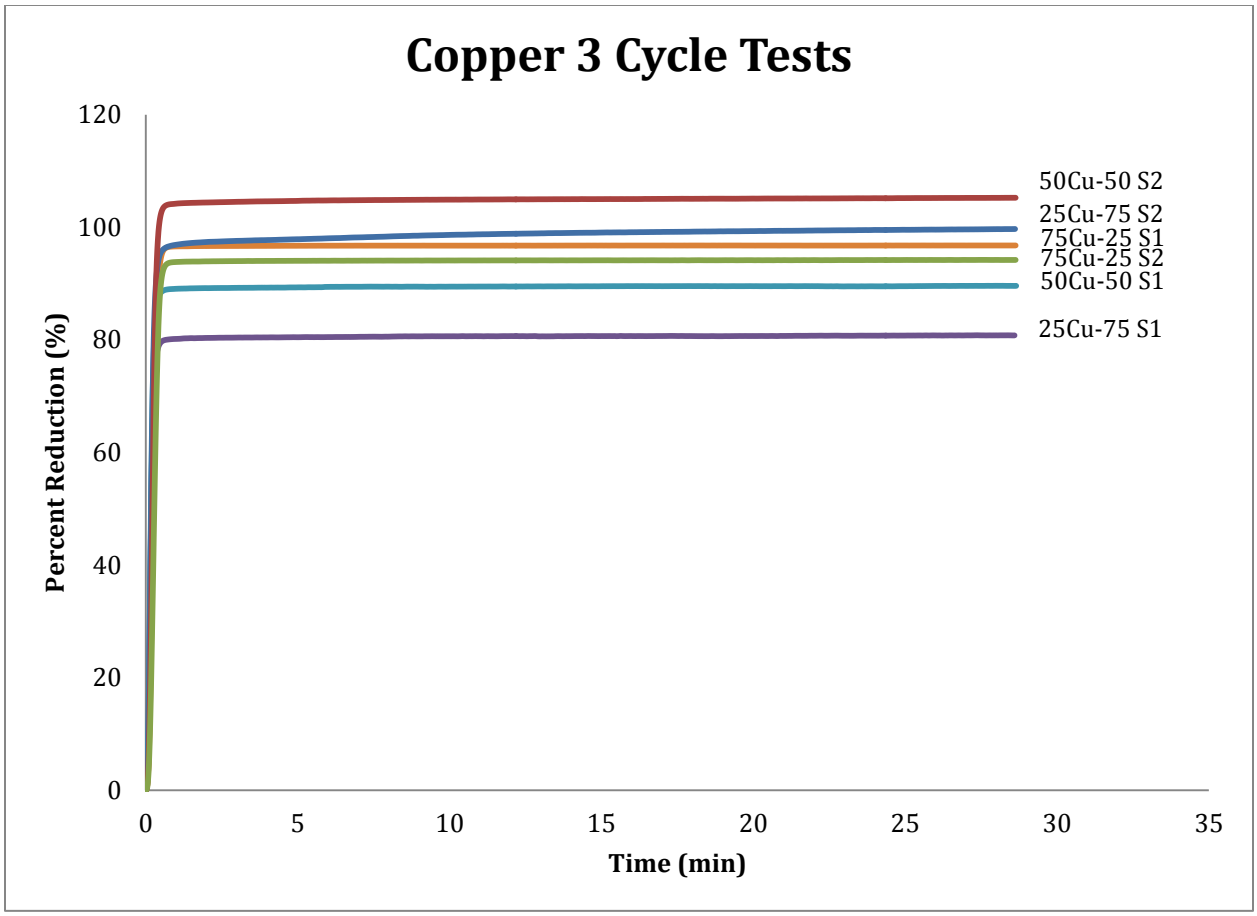

Figure 10: 3 Cycle Tests using Copper Oxide Compositions

Similar to the iron and nickel tests, S2 supports performed the best in the copper tests. Only 50%Cu – 50%S2 showed reduction over the theoretical 100%. The rates of reactivity for copper were similar for each support, although S2 supports were slightly faster again. In each case, near full reduction was achieved in less than one minute. These rates were faster than both iron and nickel compositions.

For each of the metal oxides, there was at least one composition that exhibited weight changes that exceeded the theoretical maximum. Two possible explanations for this relate back to the assumptions made when calculating the theoretical maximum oxygen carrying capacity.

Firstly, if the mixtures were not completely homogeneous and there was a higher weight percent of the metal oxide present it would result in a greater possible weight percent change. Since mechanical mixing does not make completely homogeneous solution this is a likely source of error. Secondly, it was assumed that the support material does not exhibit any redox reactivity. However, it has been shown that S2 does exhibit some reduction reactivity at temperatures above 850°C[19]. While the reactivity of S2 is low, this would result in a slightly increased oxygen carrying capacity, thus corresponding to a weight change greater than the theoretical maximum. S1 has not been shown to have this type of redox reactivity, so the original assumptions should still be valid for these mixtures. Compositions containing S2 as the support showed higher degrees of reduction than those containing S1, which can be partly attributed to its slight redox reactivity.

Using the change in weight over time curves for the various compositions the initial rate of reduction could be calculated. This was done by measuring the initial reduction slope where the reduction rate is at maximum. Shown in Table 3 (on the following page) are the rates of reduction for the third cycle for all compositions tested in units of mg/min. Overall the copper mixtures reduced with the highest rate, followed by nickel and then iron. Also, increasing the amount of metal oxide for each composition resulted in faster reduction. In comparing only the two supports, the mixtures containing S2 reduced at a higher rate. This could partially be due to the fact that S2 shows a small degree of redox reactivity at high temperatures. The rate of reduction is important when considering the particle composition because it determines the residence time of the particles in the reactor. Higher reaction rates correspond to shorter times in the both the reducer and oxidizer reactors.

Table 3: Reaction rates of different compositions (in mg/min)

		Fe_2O_3		Nickel		Copper	
		S1	S2	S1	S2	S1	S2
Composition (MO:Support)	25:75	1.69	3.13	2.20	3.88	2.59	5.39
	50:50	2.27	5.15	5.20	10.43	3.43	10.02
	75:25	4.31	5.66	7.10	14.23	12.15	15.58

3.3 Ten Cycle Testing

To conduct the first series of longer cycle tests, the six 50:50 weight percent compositions were tested for 10 cycles. Similar to the 3 cycle tests, the percent reduction was calculated, this time, however, it was done for each cycle. Once the percent reduction curve was generated the maximum percent reduction for each cycle could be obtained. Figure 11 shows the maximum percent reduction for each cycle for each of the six compositions tested.

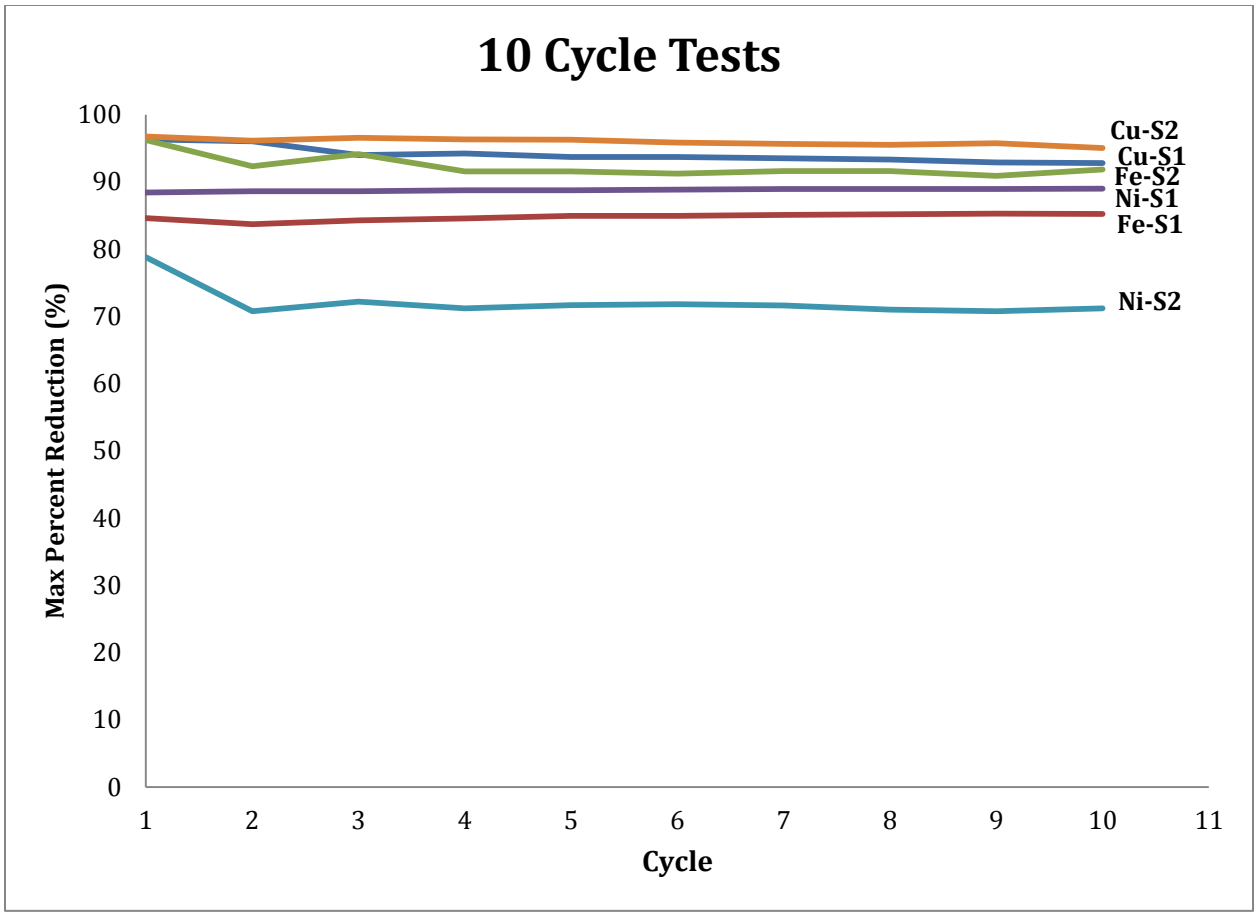

Figure 11: Maximum percent reduction obtained each cycle for 10 cycle tests

Overall, all the metal oxides performed well and showed little degradation over 10 cycles. The Ni-S2 composition showed the greatest loss in performance of all the compositions, at approximately 8% of the maximum percent reduction. Fe-S2 also exhibited performance degradation over time, although not as much as Ni-S2. While the S2 compositions of iron and nickel showed performance degradation over time, the S1 compositions of both metal oxides were among the most stable and exhibited nearly zero change in reactivity. One possible explanation for this result is the formation of complexes with the S2 support. If the metal oxide is complexed with S2 the overall oxygen capacity would be lowered, accounting for the loss in reactivity over time.

3.4 Twenty Cycle Testing

To further test the long-term recyclability of the different particle compositions, the three 50:50 weight percent that contained S2 as the support material were run for 20 cycles. Then,similar to the 10 cycle testing, the maximum percent reduction was calculated for each cycle. Figure 12 shows the maximum percent reduction for each cycle.

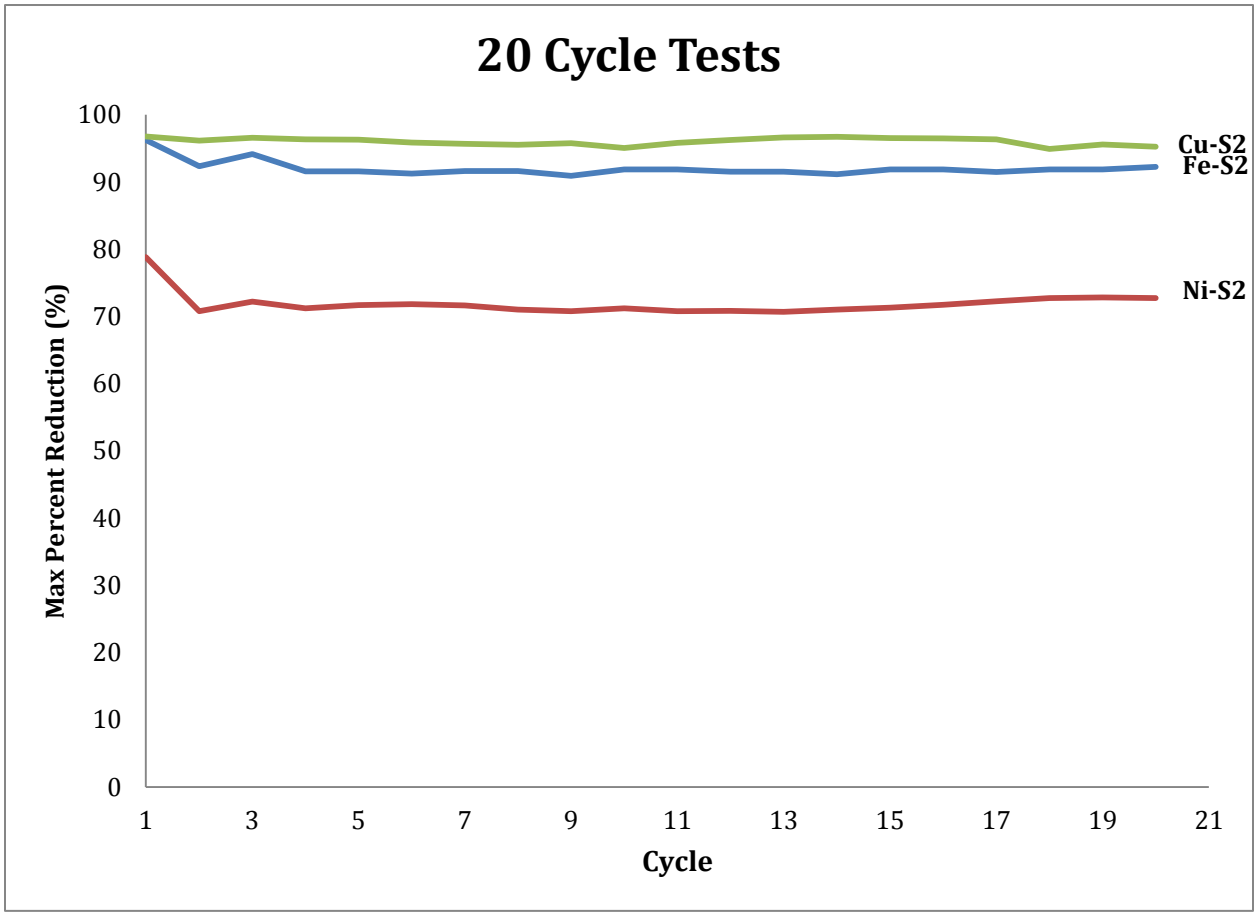

Figure 12: Maximum percent reduction obtained each cycle in 20 cycle tests

Similar to the 10 cycle tests, all three compositions showed little degradation of reduction reactivity over time. Ni-S2 again showed the largest loss in performance, followed by Fe-S2. In terms or long term reactivity Cu-S2 would be the best choice, although realistically any of the three compositions would be appropriate.

3.5 Biomass Testing

The six 50:50 weight percent compositions were used to test reactivity in the presence of biomass char. These tests were run for one cycle and the percent reduction was measured. Figure 13 shows the reduction curve for each of the compositions.

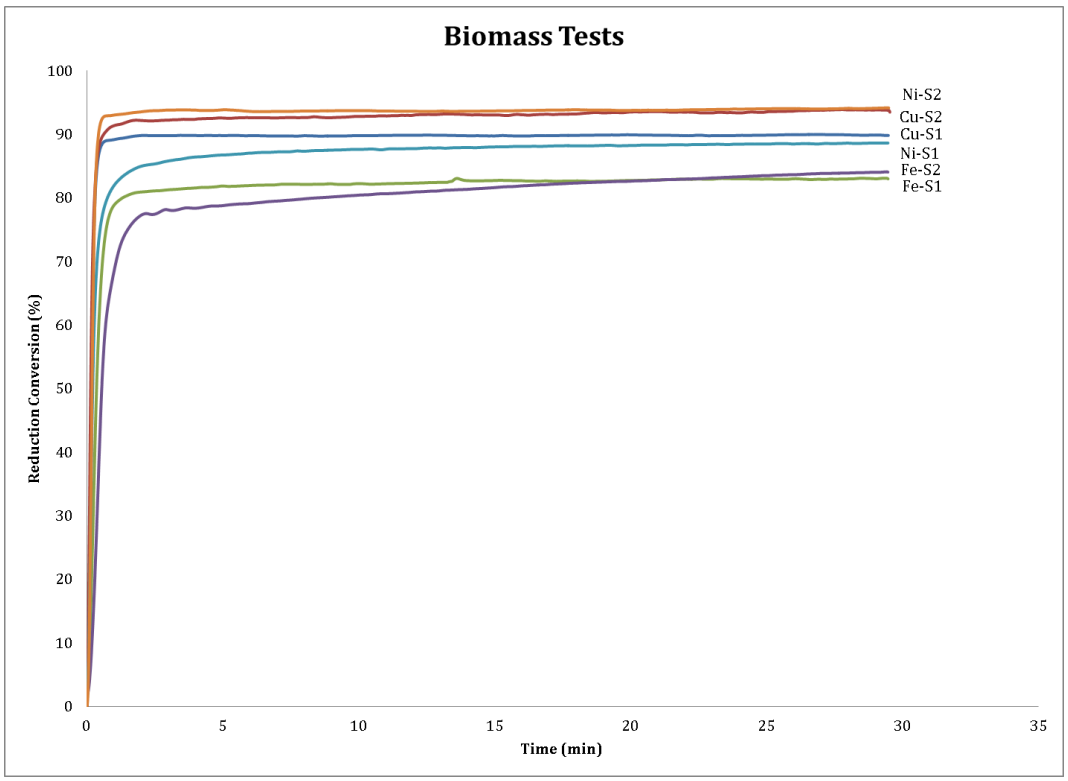

Figure 13: Biomass conversion for each 50:50 weight percent composition

Similar to the three cycle tests, the reduction rates were also calculated. These are shown in Table 4 below.

Table 4: Reduction rates for biomass tests (in mg/min)

	S1	S2
Fe	2.66	2.77
Ni	3.41	5.91
Cu	4.37	4.32

The presence of biomass char lowered the reduction rates for every composition compared to the three cycle tests.

3.6 General Discussion

When optimizing a particle, a number of characteristics need to be considered and the importance of each characteristic must be weighed. For this study the characteristics tested were oxygen carrying capacity, reactivity (rate of reduction), long-term recyclability, and reactivity with biomass char. When choosing the optimum particle other outside characteristics, such as price and environmental impact, need to be considered as well. Although no composition exhibits the best of all of these characteristics, an optimum particle will have minimum drawbacks while still being an effective oxygen carrier.

Iron based particles have the highest oxygen carrying capacity and good long-term recyclability, yet the rate of reduction was slower than either nickel or copper based particles. Although the reduction rate was slower, the rate was still large enough that the chemical looping process could be run efficiently. An economic benefit for Fe_2O_3 is that it is the most inexpensive of the three metal oxides. When comparing chemical looping used to repower a coal-fired power

plant or used in replacement of a traditional boiler to a traditional pulverized coal-fired power plant, one of the largest capital costs would be the operating cost associated with the oxygen carrying particles. Fe_2O_3 particles would thus be an economical choice.

NiO compositions have moderate oxygen carrying capacity, and good reactivity, yet are toxic to the environment and expensive. The moderate oxygen carrying capacity means that more particles will be needed, which correlates to larger-sized reducer and oxidizer reactors. Also, the toxicity of NiO is a drawback, since this technology is being developed as an environmentally friendly option; thus, solids handling of nickel waste would be an issue to consider. While the nickel compositions do have some disadvantages, they did perform well in all the tests.

CuO compositions have excellent reactivity and show little loss in reactivity in long-term testing, yet have the smallest oxygen carrying capacity, a low melting point, and are expensive. The small oxygen carrying capacity results in a problem similar to NiO, meaning more particles will be required. Also due to the high demand of copper, the price for CuO is high; meaning that the operating costs from replacing particles will be high. However, perhaps the most significant disadvantage for CuO is its low melting point. The reactions taking place in the oxidizer are highly exothermic, which can result in areas of extra high temperature in the reactor. In these places of extra high temperature the copper can melt, resulting in large agglomerations. These agglomerations are unreactive and can result in undesirable blockages throughout the system. Thus, the reactor operation would be difficult.

In terms of support material, S2 aided reactivity of the all the metal oxides more than S1. In nearly every trial, compositions containing S2 not only achieved higher levels of reduction but did so at faster rates than the S1 compositions. While reactivity is of primary importance, the

mechanical strength of the particles is also of importance. For future studies, this should also be taken into consideration along with different particle preparation methods.

Overall the compositions containing CuO and NiO were determined to be the optimum particles in terms of reactivity. Both showed good reactivity through all the tests. Copper compositions had slightly better kinetics, however, the nickel compositions were close behind.

4. Conclusions

Finding energy stability from renewable energy sources while mitigating anthropogenic CO_2 emissions is one of the great problems of the current generation. Coal, natural gas, and oil are widely available now, but combined emit billions of tons of CO_2 into the atmosphere each year, and, ultimately, are unsustainable energy sources. Chemical looping combustion is an emerging technology that has potential to clean up emissions from coal efficiently with minimum economic penalty. The chemical looping combustion technology could theoretically be extended to a lignocellulosic fuel, resulting in a clean and renewable energy source.

Fundamental to chemical looping are oxygen carrying particles. This study focused on testing screening particles made of the metal oxides or iron, nickel, and copper, combined with two supports, which are referred to as S1 and S2. The different composition ratios of the particles tested were by weight percent 25:75, 50:50, and 75:25 (metal oxide:support). Characteristics of these particles that were tested include oxygen carrying capacity, reactivity, recyclability, and reactivity with biomass char. Additional characteristics that were considered were cost and environmental impact.

Of the three metal oxides, copper compositions showed the highest rates of redox reactivity and also the lowest loss in performance in long-term testing. While iron and nickel did not exhibit reduction rates as high as copper, both displayed good reactivity and comparable performance. Also, iron was calculated to have the highest oxygen carrying capacity, followed by nickel and finally copper.

In terms of reactivity the optimum particle composition would contain either CuO or NiO as the metal oxide and S2 as the support material. Compositions containing these components showed fast reaction kinetics, good reactivity over many cycles, and good reactivity in the presence of biomass char.

Although the CuO and NiO compositions exhibited many characteristics of an optimum oxygen carrying particle, more work must be done to obtain the correct ratio of metal oxide to support. Also, another characteristic that must be compared is the strength and attrition resistance of different compositions. In this study, S2 was determined to be a better supporting material because it aided reactivity; however, it must still be able to provide mechanical strength to the particle.

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